

# PATENT SPECIFICATION

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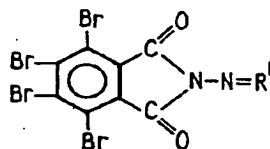
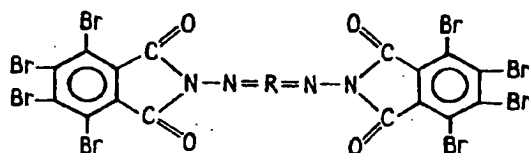
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## (54) TETRABROMOPHTHALIMIDE DERIVATIVES AND THEIR USE AS FLAMEPROOFING AGENTS

(71) We, DYNAMIT NÖBEL AKTIENGESellschaft, a German Company of 521 Troisdorf bez Köln, postfach 1209, Germany do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

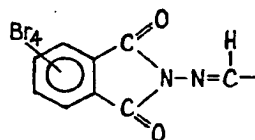
5 This invention relates to tetrabromophthalimide derivatives and to their use as flameproofing agents. 5

According to the present invention, the tetrabromophthalimide derivatives of the invention are azomethine imides having the general formulae (I) or (Ia):



in which R is a radical derived from a dialdehyde and R' is a radical derived from a monoaldehyde.

The azomethine imides according to the invention may therefore be regarded as acyl hydrazones of monoaldehydes and as bis-acyl hydrazones of dialdehydes corresponding to the general formula B-A-B' where B has the meaning



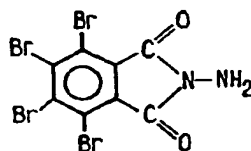
B' has the meaning H or B and A has the meaning of an aliphatic straight-chain or branched, preferably saturated C<sub>0</sub>-C<sub>25</sub>, preferably C<sub>0</sub>-C<sub>4</sub> radical which does not contain the

40

carbon atom of the aldehyde group or both aldehyde groups, or the meaning of an aromatic radical, preferably the benzene ring, which is optionally substituted, particularly by alkyl.

The azomethine imides are useful as flameproofing agents (FP-agents) for plastics.

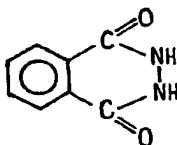
The bromine-containing azomethine imides are derived as Schiff's bases from N-aminotetrabromophthalimide corresponding to structural formula (IV) below



(IV)

and monoaldehydes or dialdehydes such as, for example, formaldehyde, isobutyraldehyde, glyoxal or terephthalaldehyde. The N-aminotetrabromophthalimide corresponding to formula (IV) may surprisingly be obtained in pure form and in good yields from tetrabromophthalic acid anhydride and hydrazine.

It was already known that phthalic acid anhydride and hydrazine could be reacted in the presence of solvents, for example acetic acid, to form phthal-2,3-diaza-1,4-dione, a diazadione corresponding to the structural formula below:



According to H. Drew and H. Hatt, J. Chem. Soc. (1937), page 16, a hydrazide carboxylic acid is initially formed from equimolar quantities of phthalic acid anhydride and hydrazine, reacting in boiling acetic acid to form only the diazadione. According to Drew and Hatt, mixtures of phthal-2,3-diaza-1,4-dione with small amounts of N-amino-phthalimide are formed with reaction times of a few minutes, although we were unable to confirm this.

According to J. I. Jones, J. Polymer Sci., Part C, 22 (1969), page 773, the reaction of benzophenone-3,4,3',4'-tetracarboxylic acid dianhydride with an excess of hydrazine hydrate results exclusively in the formation after only 10 minutes of diazadiones in the form of corresponding bis-diazadiones which are obtained in high yields.

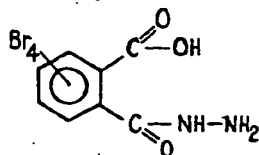
By contrast, the reaction of tetrabromophthalic acid anhydride with hydrazine as hydrate in glacial acetic acid as solvent surprisingly results in the exclusive formation of N-aminotetrabromo-phthalimide corresponding to structural formula (IV) in substantially quantitative yields, particularly where a molar excess of hydrazine is used, both with short and also with prolonged reaction times.

Tetrabromophthalic acid anhydride and hydrazine may be used in a molar ratio of 1:1. Alternatively, hydrazine may be used in a molar excess of up to 1:2 or even higher. A local excess of the tetrabromophthalic acid anhydride should be avoided because it results in formation of the unwanted N-tetrabromophthalimidotetrabromophthalimide.

Even where the two reactants are used in an equivalent ratio, an excess of the tetrabromophthalic acid anhydride is avoided simply by reacting the hydrazine hydrate with a suspension of the tetrabromophthalic acid anhydride in a solvent or solvent mixture. This result is achieved either by adding the hydrazine to a suspension of the tetrabromophthalic acid anhydride in, preferably, glacial acetic acid or a mixture of glacial acetic acid and o-dichlorobenzene at temperatures of from 0 to 150°C and preferably at temperatures of from 20 to 40°C, or by introducing the tetrabromophthalic acid anhydride in portions into a solution of the hydrazine hydrate in one of the above-mentioned solvents. In the latter case, the hydrazine is present as equally reactive hydrazine acetate.

If desired, brominated phthalic acid anhydride with a fairly low degree of bromination, for example in the form of tribromophthalic acid anhydride, or with small chlorine contents in addition to a high bromine content may be used for the reaction.

In both cases, the hydrazide carboxylic acid



is initially formed from tetrabromophthalic acid anhydride, and is then cyclodehydrated by an increase in temperature to form the required N-aminotetrabromophthalimide (IV). It is of advantage to increase the reaction temperature to levels at which the water of reaction can be removed from the system by distillation under normal pressure over a reaction time of 1 to 3 hours, i.e. to between 115 and 150 and preferably to between 115 and 130°C.

The N-aminotetrabromophthalimide is obtained in the form of an insoluble finely crystalline product pale yellow-green in colour and may be isolated by filtration under suction and washing, for example with methanol, and dried. The product which has a melting point of 295 - 298°C with incipient decomposition is so pure that it does not have to be purified any further for the desired reaction with the aldehydes to form the Schiff's base.

The amino group of the N-aminotetrabromophthalimide is only weakly basic on account of the adjacent imide structure. Accordingly, it is not the acetate, but instead the compound of formula (IV) containing a free amino group which is formed during the synthesis in acid solution, for example glacial acetic acid, or a solution containing glacial acetic acid or acetic acid.

Despite the limited basicity of the  $\text{NH}_2$ -group, the N-aminotetrabromophthalimide surprisingly reacts readily with aldehydes to form the azomethine imides.

To this end, the two reactants in a molar ratio of N-aminotetrabromophthalimide to aldehyde of 2:1 in the case of dialdehydes or 1:1 in the case of monoaldehydes, optionally with a small excess of the aldehydes of up to 20 %, are heated to temperatures in the range from 80 to 200°C, preferably from 100 to 190°C, in a solvent or solvent mixture, preferably *o*-dichlorobenzene or a mixture of glacial acetic acid and *o*-dichlorobenzene, the water of reaction formed during formation of the azomethine advantageously being removed from the reaction system, optionally together with some of the solvent or solvent mixture. In general, the bromine-containing azomethine imides or acyl hydrazones according to the invention are obtained in insoluble form and, after the suspension has cooled, may be filtered off under suction, washed out, preferably with methanol, and dried.

The reaction is preferably carried out under normal pressure although if desired, pressures of up to 10 bars may be applied.

Suitable aldehydes are basically any monoaldehydes and dialdehydes. It is preferred to use the aldehydes containing the above-mentioned residue A, of which those obtainable as commercial products are particularly preferred. Examples of these aldehydes include formaldehyde, acetaldehyde and propionaldehyde, the isomeric butyraldehydes, benzaldehyde and tolyl aldehydes, glyoxal, terephthal-dialdehyde and isophthalaldialdehyde, optionally even halogenated aldehydes, such as chlorobenzaldehyde, tetrabromoterephthalaldehyde and, with limitations, chloral.

The substances are obtained in a purity which is sufficient for the desired purpose and do not have to be subsequently purified.

For economically producing the azomethine imides or acyl hydrazones (I) and (Ia) according to the invention, it is of considerable advantage that the intermediate product, N-aminotetrabromophthalimide (IV), formed after the first stage of the reaction does not have to be isolated, dried and reused for the reaction with the aldehydes. Instead, it is possible to add the aldehyde or dialdehyde to the suspension of the N-aminotetrabromophthalimide formed after the first stage of the reaction and directly to carry out the second stage of the reaction leading to the end product (I) or (Ia). A mixture of glacial acetic acid and *o*-dichlorobenzene in a ratio by volume of 5/95 to 25/75 is preferably used as solvent for this two-stage "one-pot process". During the first stage, most of the acetic acid may be distilled off with the water of reaction so that the second stage takes place in *o*-dichlorobenzene.

The bromine-containing azomethine imides of the present invention are useful flameproofing agents for plastics materials. Accordingly, the present invention includes flameproofed plastics moulding compositions comprising as flameproofing agent, the bromine-containing phthalimides of formulae I and/or Ia, optionally together with synergistically acting additives, such as antimony trioxide.

Suitable quantities are quantities as small as 3 to 20% by weight, preferably 5 to 15% by weight, based on the polymeric component of the plastics.

Any plastics may be used for producing the moulding compositions. Thus, it is possible to

use polymerisation plastics of mono- or di-olefins such as ethylene, propylene, butene, styrene, vinyl compounds such as vinyl chloride, vinyl acetate, et., copolymers and graft polymers thereof with one another and, for example, with acrylonitrile, alkyl (meth)acrylates and diolefins such as butadiene or isoprene; polyesters, optionally polyamides, cellulose plastics and their derivatives; polycondensation plastics such as phenolic resins, urea and melamine resins, epoxy resins and others.

High-melting plastics which are processed at high temperatures, particularly high-melting polycondensates such as high-melting, optionally linear polyesters, polycarbonates, high-melting polyamides, polyurethanes and optionally their mixtures with one another or with other polymers and copolymers, are especially suitable.

The azomethine imides can be worked without difficulty into the plastics material, for example on mixing rolls or in extruders, show adequate thermal stability during processing, i.e. do not give rise to discoloration or fuming at the processing temperatures, are effective flameproofing agents and do not subsequently chalk out of the plastics. They also have little or no effect upon the mechanical, thermal and electrical properties of the plastics and are simple and economic to produce.

The structure of the azomethine imides might have been expected to give rise to an extensive reaction during their incorporation into thermoplastic polyesters, for example PTMT in the melt at temperatures in the range from 220 to 250°C, accompanied by substantial degradation of the chain. Surprisingly, however, only minimal degradation occurs. The reduction in the reduced specific viscosity of PTMT during incorporation of the flameproofing agent amounts to between 0.3 and 0.4 dl/g for an initial value of from 1.5 to 1.6 dl/g the reduction in viscosity attributable to the flameproofing agent amounting to between 0.15 and 0.25 dl/g.

Surprisingly, the bromine-containing phthalimides corresponding to structural formulae I and Ia do not chalk out from a number of plastics, including *inter alia* polyethylene terephthalate, polytetramethylene terephthalate and also polymers, although the compounds in question are neither high molecular weight or crosslinked compounds nor compounds which are anchored to the matrix by homopolar bonds, but instead are low molecular weight powder-form flameproofing agents.

In contrast to known flameproofing agents, the agents according to the invention are highly stable at elevated temperatures. At 150°C, the weight loss is negligible, even after several weeks.

The comparatively high bromine content of more than 60% by weight of most of the azomethine imides, in conjunction with the nitrogen content of the imide structure, also provides for adequate flameproofing despite a reduction in the amount of flameproofing agent in relation to conventional flameproofing agents. The azomethine imides according to the invention show outstanding thermal stability so that they withstand the processing and service temperatures even of constructional materials without decomposing or discolouring. These flameproofing agents which are obtained in the form of fine-grained powders during their actual synthesis may readily be worked into the thermoplasts to be flameproofed on mixing rolls or in extruders. In addition, the extremely poor solubility of these substances in almost all solvents prevent the flameproofing agents from dissolving out when the flameproofed plastics according to the invention come into contact with liquid media. Due to the small grain size and the resulting optimum distribution and large surface activity of the flameproofing agents in the matrix, the reduction in the mechanical properties of the flameproofed plastics is minimal. Another advantage of the flameproofing agents according to the invention is that they do not produce any reduction in melting point in the case of crystalline thermoplasts, such as PTMT, so that plastics such as these retain their property spectrum and can still be produced by post-condensation in the solid phase.

The invention will now be illustrated by the following Examples. In the Examples, reference is made to the Underwriters Laboratories UL94 Test. In this Test, the terms V0, V1, V2 and V3 have the following meanings:

VO means that the average after-burning time of the test specimen is 5 seconds or less and that the highest after-burning time is not more than 10 seconds.

V1 means that the average after-burning time is less than 25 seconds and that the highest after-burning time is not more than 30 seconds;

V2 means that the after burning time is less than 25 seconds but that dripping pieces of plastic result; and V3 means that the specimen is not self-extinguishing.

#### EXAMPLE 1

##### *Production of N-aminotetrabromophthalimide (Structural Formula IV)*

1250 ml of glacial acetic acid are introduced into a reaction vessel equipped with a paddle stirrer, a Vigreux column surmounted by a distillation bridge and a gas inlet pipe, followed by the gradual addition with stirring of 100 g (2 moles) of hydrazine hydrate. 464 g (1 mole)

of tetrabromophthalic acid anhydride are introduced in portions into this solution of the hydrazine hydrate while stirring and passing over nitrogen. On completion of the addition, the mixture is heated to 110 - 120°C so that a mixture of acetic acid and water distills over at a moderate distillation rate and the water of reaction is removed. After 2 hours, the reaction is over and the reaction product is in the form of a pale yellow-green suspension. After cooling, the reaction product is filtered under suction, washed twice with methanol and dried at up to 170°C.

443 g of N-aminotetrabromophthalamide are obtained. Yield 92.6 %. Melting point upwards of 295°C with incipient decomposition and a change in colour to red-brown.

According to the IR-spectrum, the product is N-aminotetrabromophthalamide (IV) since bands of the C=O and primary valency bands appear at 1700, 1720/1770 and at 3180, 3245 and 3325 cm<sup>-1</sup> and because there are no indications of secondary amides.

Elemental analysis:	observed	C 20.51	calculated	C 20.10
	H 0.40		H 0.41	
	N 5.86		N 5.85	
	Br 66.8		Br 66.9	

The weight loss after storage under heat (24 hours in air at 200°C) amounts to 0.38 %. According to TGA (air atmosphere; heating 8°C/minute), the weight loss amounts to 1 % at 290°C, to 5 % at 303°C, to 10 % at 320°C and to 20 % at 347°C.

The N-aminotetrabromophthalamide is substantially insoluble in the usual solvents at room temperature and only very sparingly soluble at higher temperatures. No salt formation occurs with aqueous hydrochloric acid or with glacial acetic acid, as was shown by IR and elemental analysis.

#### EXAMPLE 2:

*Production of the bromine-containing azomethine imide of formula (I) with R = =CH-CH= from N-aminotetrabromophthalamide*

In a reaction flask equipped with a dropping funnel, blade stirrer, distillation bridge and gas inlet pipe, 190.8 g (0.4 mole) of N-aminotetrabromophthalamide (IV) are suspended in 400 ml of *o*-dichlorobenzene, followed by the addition with stirring of 38.6 g of a 30 % aqueous glyoxal solution (= 0.2 mole of glyoxal). While a gentle stream of nitrogen is passed over, the reaction mixture is heated to 140°C so that the water added and the water formed during the reaction distill over together with part of the *o*-dichlorobenzene. The *o*-dichlorobenzene is replaced by dropwise addition from the dropping funnel at a rate commensurate with the distillation rate. The temperature is further increased to 180°C until, towards the end of the reaction, the *o*-dichlorobenzene distills over on its own. After a total reaction time of 2.5 hours, the suspension formed is allowed to cool, the product is filtered off under suction and washed three times with methanol. After working up in the same way as in Example 1, the reaction product is obtained in the form of a substantially colourless powder. Yield 187.6 g, corresponding to 95.9 % of the theoretical. Melting point > 320°C; no colour or morphological change up to 320°C.

In the IR-spectrum, the NH-stretching vibrational bands of the starting products N-aminotetrabromophthalamide (IV) have disappeared. The cyclic imide function  $\nu(\text{C}=\text{O}) = 1730, 1735 \text{ cm}^{-1}$  has remained intact.

Elemental analysis:	observed	C 22.62	calculated	C 22.10
	H 0.24		H 0.20	
	N 5.75		N 5.72	
	Br 65.1		Br 65.4	

The weight loss after storage under heat (3 hours and 24 hours in air at 200°C) amounts to 0.18 % and 0.37 %, respectively.

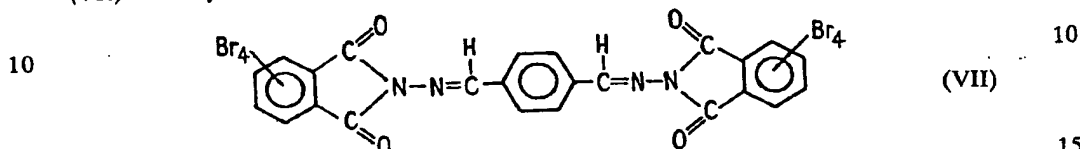
The sample shows no visual change after storage. According to TGA (air atmosphere; heating rate 8°C/minute), the weight loss amounts to 1 % at 371°C, to 5 % at 400°C, to 10 % at 407°C and to 20 % at 410°C.

The bromine-containing azomethine imide of formula (I) with R = =CH-CH= is substantially insoluble in most organic solvents at room temperature. Under heat, it shows

very slight solubility in some aprotic polar solvents, such as dimethyl formamide, dimethyl acetamide, dimethyl sulphoxide, hexamethyl phosphoric acid triamide or N-methyl pyrrolidone.

5 **EXAMPLE 3:**

*Production of the bromine-containing azomethine imide corresponding to structural formula (VII) below from N-aminotetrabromophthalimide and terephthal dialdehyde*



15 In a reaction flask equipped in the same way as in Example 2, 89.7 g (0.2 mole) of N-aminotetrabromophthalimide are suspended in 130 ml of *o*-dichlorobenzene, followed by the addition of 13.4 g (0.1 mole) of terephthal dialdehyde. The reaction mixture is heated with stirring under nitrogen until the water of reaction distills over together with 20 part of the *o*-dichlorobenzene. The bath temperature is further increased to 190°C so that, towards the end of the reaction, *o*-dichlorobenzene distills over and is replaced by the dropwise addition of 20 ml.

25 After 2.5 hours, the reaction is stopped, the suspension formed is allowed to cool and the reaction product is filtered off under suction, washed with methanol and dried at up to 180°C. A fine, pale yellow powder of the substance of formula (VII) is obtained. Yield: 98.8 g, corresponding to 93.7 % of the theoretical. Melting point > 320°C; no visual change in the sample up to 320°C.

30	Elemental analysis:	calculated	C 27.48	observed	C 27.32	30
			H 0.61		H 0.57	
			N 5.35		N 5.31	
			Br 60.3		Br 60.7	

35 Weight loss (in air at 200°C): 0.26 % after 3 hours and 0.49 % after 24 hours. The sample remains unchanged.

40 According to TGA (air atmosphere; heating rate 8°C/minute/, the weight loss amounts to 1 % at 362°C, to 5 % at 386°C, to 10 % at 398°C and to 20 % at 406°C.

The azomethine imide is only slightly soluble in a few aprotic polar solvents, and even then only with heating.

45 **EXAMPLE 4:**

*Bromine-containing azomethine imide from tetrabromophthalic acid anhydride, hydrazine and glyoxal*

45 In a reaction flask equipped in the same way as in Example 2, 5.0 g (0.1 mole) of hydrazine hydrate are dissolved in a solvent mixture of 20 ml of glacial acetic acid and 180 ml of *o*-dichlorobenzene (ratio by volume 10/90). 46.4 g (0.1 mole) of tetrabromophthalic acid anhydride are introduced with stirring. The reaction temperature is increased to 130°C 50 while a gentle stream of nitrogen is passed over, so that approximately 15 ml of distillate (acetic acid + water) distill over in 2 hours.

55 After cooling, 9.68 g of a 30 % aqueous glyoxal solution ( $\approx$  0.05 mole of glyoxal) are added to the suspension of the N-aminotetrabromophthalimide and the reaction temperature is increased over a period of 1 hour to 190°C (bath temperature), at which first water and a residue of acetic acid, then water and *o*-dichlorobenzene and, towards the end, *o*-dichlorobenzene, in all 65 ml, distill off over a period of 3 hours.

The addition of the glyoxal solution to the hot (130°C) suspension of N-aminotetrabromophthalimide leads to the same result.

60 After the suspension has cooled, the reaction product is filtered off under suction, washed with methanol and dried at up to 180°C. A dust-fine powder with a tinge of ochre in its colour is obtained.

Yield: 45.2 g, corresponding to 92.4 %.

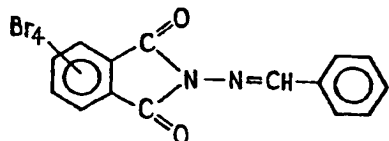
Melting point > 320°C; no visual change in the sample up to 320°C.

65 According to the IR-spectrum, the substance is identical with the substance of Example 65

2. Elemental analysis, weight loss in air and according to TGA and also the solubility levels correspond to the substance according to Example 2.

#### EXAMPLE 5

5 *Bromine-containing azomethine imide corresponding to structural formula (VIII) below 5 from tetrabromophthalic acid anhydride, hydrazine and benzaldehyde*



(VIII)

15 In the reaction vessel described in Example 2, 5.0 g (0.1 mole) of hydrazine hydrate are 15 dissolved in 150 ml of glacial acetic acid and 46.4 g (0.1 mole) of tetrabromophthalic acid anhydride are added in portions with stirring to the solution of the hydrazine hydrate at room temperature while a gentle stream of nitrogen is passed over. The reaction mixture is heated to 120 - 140°C, approximately 30 ml of distillate (acetic acid + water) distilling over in 2 hours, being replaced by the dropwise addition of 30 ml of glacial acetic acid. After cooling to approximately 60°C, 10.6 g (0.1 mole) of benzaldehyde are added and the reaction mixture is reheated to 130°C - 150°C so that approximately 40 ml of distillate distill off under suction, washed with methanol and dried at 120°C and then for 2 hours at 180°C. 20  
25 A fine, pale yellowish powder is obtained. Yield: 52.8 g, corresponding to 93.3%. Melting point: 272 - 276°C; no visible change beforehand. 25

30	Elemental analysis:	observed	C 30.95	calculated	C 31.80	30
			H 1.05		H 1.06	
			N 4.86		N 4.94	
35			Br 56.5		Br 56.5	35

The weight loss of a sample in air at 200°C amounts to 0.15 % after 3 hours and to 0.35 % after 24 hours.

40 According to TGA (air atmosphere; heating rate 8°C/minute), the weight loss amounts to 1 % at 338°C, to 5 % at 371°C, to 10 % at 383°C and to 20 % at 396°C 40

#### EXAMPLE 6:

*Bromine-containing azomethine imide corresponding to formula (Ia) with R' = =CH<sub>2</sub>*

45 In a reaction vessel equipped in the same way as described in Example 5 and following the procedure of that Example, 139.2 g (0.3 mole) of tetrabromophthalic acid anhydride are reacted with 15.0 g (0.3 mole) of hydrazine hydrate in 340 ml of a mixture of glacial acetic acid and *o*-dichlorobenzene (ratio by volume 20/80) as solvent to form N-aminotetrabromophthalimide, which, without isolating the intermediate product, is directly 50 reacted with 9.9 g (0.33 mole) of formaldehyde in the form of paraformaldehyde. After filtration under suction, washing with methanol and drying of the azomethine imide add up to 180°C, a substantially colourless powder corresponding to formula (2) with R' = =CH<sub>2</sub> is isolated in a yield of 136.7 g, corresponding to 93 % of the theoretical. Melting point: 295 - 299°C. 50

55 According to the IR-spectrum, the imide function of the intermediate product, N-aminotetrabromophthalimide, is still intact in the end product, whereas NH-stretching vibrational bands do not appear in the product. 55

	Elemental analysis:	observed	C 22.63	calculated	C 22.04	
			H 0.28		H 0.40	
5			N 5.44		N 5.71	5
			O 6.47		O 6.50	
			Br 65.2		Br 65.3	
10						10

#### EXAMPLE 7

Following the procedure of Example 6, a bromine-containing azomethine imide corresponding to formula (Ia) with  $R' = \text{CH-CH(CH}_3)_2$  is produced from 10.0 g (0.2 mole) of hydrazine hydrate, 92.8 g (0.2 mole) of tetrabromophthalic acid anhydride and 14.4 g (0.2 mole) of isobutyraldehyde. Yield: 94.6 g, corresponding to 88.8 % of the theoretical. Melting point:  $> 320^\circ\text{C}$ ; no visible change in the sample up to  $320^\circ\text{C}$ .

	Elemental analysis:	observed	C 26.95	calculated	C 27.06	
25			H 1.45		H 1.50	25
			N 5.10		N 5.26	
			Br 59.0		Br 60.2	30

#### EXAMPLES 8 and 9

A mixture consisting of 86 % by weight of PTMT (polytetramethylene terephthalate, strand granulate, reduced viscosity (1 % solution in a 60/40 mixture of phenol and *o*-dichlorobenzene at  $25^\circ\text{C}$ ) = 1.60 dl/g, 10 % by weight of the bromine-containing azomethine imide of Example 2 and 4 % by weight of  $\text{Sb}_2\text{O}_3$ , is extruded in a twin-screw extruder at  $245$  to  $255^\circ\text{C}$  to form a strand.

Processing does not present any difficulties. There was no sign either of fuming or of discoloration. The reduced viscosity of the PTMT component in the extruded strand has undergone a comparatively small decrease to 1.46 dl/g.

According to DTA (heating rate  $8^\circ\text{C/minutes}$ ), the melting point of the PTMT component in the extruded strand lies at  $216^\circ\text{C}$  (TSP/ $226^\circ\text{C}$  (max), i.e. is in the range of the pure PTMT.

The extruded strand is granulated and injection moulded into test specimens measuring  $127 \times 12.7 \times 1.6$  mm for the Underwriters Laboratories Test UL 94 (Example 8).

A mixture of 56 % by weight of PTMT, 30 % by weight of 6 mm long glass fibres, 10 % by weight of the substance of Example 2 and 4 % by weight of  $\text{Sb}_2\text{O}_3$  is extruded twice in a single-screw extruder at  $230$  to  $250^\circ\text{C}$  and granulated. Test specimens are produced in the same way as in Example 8 (Example 9).

The test specimens are subjected to the UL 94 fire test immediately after production and after storage for 14 days at  $70^\circ\text{C}$ . The surface of the test specimen is inspected for the chalking out of flameproofing agents. In addition, test specimens were stored in air at  $150^\circ\text{C}$  for a period of 28 days in order to assess the weight loss and to see if any of the flameproofing agent had diffused out.

The results are set out in Table 1.



TABLE 1

Example No.	UL 94 immediately after production	UL 94 after 14 days at 70°C	Oxygen index immediately after production (LOI)	Surface after 14 days at 70°C	Surface coating after 28 days at 150°C	Weight loss <sup>1)</sup> % after 7 days at 150°C	Weight loss <sup>1)</sup> % after 14 days at 150°C	Weight loss <sup>1)</sup> % after 28 days at 150°C
8	VO	VO	30.0	unchanged <sup>2)</sup>	none	0.16	0.20	0.21
9	VO	VO	30.3	unchanged <sup>2)</sup>	none	0.12	0.18	0.23
10	VO	VO	.	unchanged <sup>2)</sup>	none	0.09	0.14	0.17
11	VO	VO	30.2	unchanged <sup>2)</sup>	none	0.19	0.22	0.25
13	VO	VO	28.8	unchanged <sup>2)</sup>	none	0.17	0.24	0.28
15	VO	VO	26.1	unchanged <sup>2)</sup>	none			

<sup>1)</sup> Weight loss of pure PTMT (1 mm thick moulded panel) at 150°C

<sup>2)</sup> No coating, no chalking out of the flameproofing agent

**EXAMPLE 10**

A mixture consisting of 86 % by weight of polyethylene terephthalate having a reduced viscosity of 1.35 dl/g, 10 % by weight of the flameproofing agent according to the invention of Example 2 and 4 % by weight of  $\text{Sb}_2\text{O}_3$  is extruded at 275 to 290°C in a twin-screw extruder.

Incorporation of the flameproofing agent does not present any difficulties. There is no sign either of discoloration or of decomposition fumes. The tests carried out on test specimens corresponding to Examples 8 and 9 are summarised in Table 1.

**EXAMPLE 11**

The flameproofing agent produced by direct synthesis in accordance with Example 4 is mixed in a quantity of 10 % by weight with 86 % by weight of PTMT and 4 % by weight of  $\text{Sb}_2\text{O}_3$ , the resulting mixture is processed into strand granulate under the conditions of Example 8 and the test specimens produced are tested with the results shown in Table 1.

There is no evidence of any adverse effects of the direct synthesis by comparison with the product of Example 2.

**EXAMPLE 12**

The flameproofing agent produced by direct synthesis in accordance with Example 4 was incorporated on mixing rolls in quantities of 10 % by weight and 12 % by weight, together with 4 % by weight and 5 % by weight of  $\text{Sb}_2\text{O}_3$ , into the standard commercial-grade thermoplasts polyethylene, polypropylene, EPDM (terpolymer of ethylene, propylene and the diene norbornadiene) and ABS (terpolymer of acrylonitrile, butadiene and styrene), and the rough sheet thus obtained was moulded into 1 mm thick panels.

The flameproofing effect was determined by comparing the oxygen index with the O-value for the pure plastic.

	Example 12	Thermoplast	Quantity of FP-agent	Quantity of $\text{Sb}_2\text{O}_3$	LOI	UL 94	Comparison LOI/O-value	
			% by weight	% by weight				
30								30
35	a	poly-ethylene	10	4	26.5	V2	18.5	35
	b	poly-propylene	10	4	23.3		17.3	
40	c	"	12	5	24.8		"	40
	d	EPDM	10	4	25.4	V2		
45	e	ABS	10	4	24.0		20.5	45
	f	"	12	5	25.2	V2	"	

There was no evidence in any of the test specimens of a surface coating which would indicate chalking out of the FP-agent, even after storage for 28 days at 70°C.

**EXAMPLE 13**

A mixture consisting of 86 parts by weight of PTMT, 10 parts by weight of the FP-agent corresponding to formula (7) in Example 3 and 4 parts by weight of  $\text{Sb}_2\text{O}_3$  is processed in a twin screw extruder at 240 to 255°C to form strand granulate. No fuming or discoloration occurred. The reduced viscosity of the PTMT fell only slightly from 1.60 to 1.42 as a result of processing.

The test results obtained from test specimens are shown in Table 1.

**EXAMPLE 14**

A mixture of 86 parts by weight of polyethylene, 10 parts by weight of the FP-agent according to Example 6 and 4 parts by weight of  $\text{Sb}_2\text{O}_3$  is homogenised for 10 minutes on mixing rolls at a roll temperature of 150°C and the rough sheet obtained is moulded into 1 mm thick panels.

The oxygen index amounts to 26.9. The UL 94 test (test specimen thickness 1 mm)

produces a rating of VE2/VE2 both immediately after production of the test specimens and also after storage for 14 days at 70°C. Test specimens which had been stored for 28 days at 70°C did not show any sign of surface coating which would have indicated chalking out of the FP-agent.

#### EXAMPLE 15

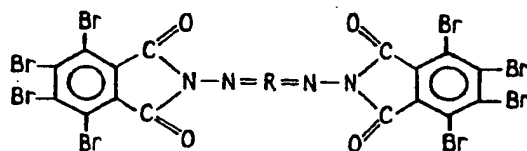
The quantity of FP-agent is reduced by 15 % in relation to Example 8. Instead of 10 % by weight, 8.5 % by weight of the bromine-containing azomethine imide of Example 2, together with 87.5 % by weight of PTMT and 4 % by weight of  $\text{Sb}_2\text{O}_3$ , are extruded, granulated and injection-moulded into test specimens under the processing conditions of Example 8.

Despite the 15 % reduction in the quantity of FP-agent, the UL 94 test produces a rating of VO.

The results of the test are shown in Table 1.

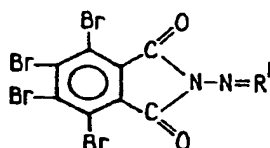
#### WHAT WE CLAIM IS:

1. A tetrabromophthalimide derivative having the general formula:



(I)

or the general formula:



(Ia)

wherein R is a radical derived from a dialdehyde and R' is a radical derived from a monoaldehyde.

2. A derivative of formula I as claimed in claim 1, wherein R is a radical derived from glyoxal, terephthaldialdehyde, isophthaldialdehyde or phthaldialdehyde.

3. A derivative of formula Ia as claimed in claim 1, wherein R' is a radical derived from benzaldehyde or an aliphatic  $\text{C}_1\text{-C}_4$  aldehyde.

4. Process for producing a tetrabromophthalimide derivative as claimed in claim 1, which comprises reacting N-aminotetrabromophthalimide with a mono- or di-aldehyde at a temperature of from 80 to 200°C.

5. A process as claimed in claim 4, wherein N-aminotetrabromophthalimide produced in a separate reaction is reacted with the mono- or di-aldehyde.

6. A tetrabromophthalimide derivative when produced by a process as claimed in claim 4 or 5.

7. A tetrabromophthalimide derivative as claimed in claim 1, substantially as described in any of Examples 2 to 7.

8. A moulding composition comprising a polymeric material and tetrabromophthalimide derivative as claimed in any of claims 1, 2, 3 and 7.

9. A moulding composition as claimed in claim 8, wherein the polymeric material is an addition polymer.

10. A moulding composition as claimed in claim 8, wherein the polymeric material is a polycondensate.

11. A moulding composition as claimed in claim 10, wherein the polycondensate is a thermoplastic linear high molecular weight polyester.

12. A moulding composition as claimed in claim 11, wherein the polyester is polyethylene terephthalate or polytetramethylene terephthalate.

13. A moulding composition as claimed in claim 10, wherein the polycondensate is a polycarbonate, a polyurethane or a polyamide.

14. A moulding composition as claimed in claim 9, wherein the addition polymer is a vinyl homopolymer or copolymer.

15. A moulding composition as claimed in claim 8, wherein the polymeric material is a

hardenable resin.

16. A moulding composition as claimed in any of claims 8 to 15, containing the tetrabromophthalimide derivative in an amount from 3 to 20% by weight.

5 17. A moulding composition as claimed in claim 16, containing the tetrabromophthalimide derivative in an amount of from 5 to 15% by weight.

18. A moulding composition as claimed in any of claims 8 to 17, additionally including a synergistically acting substance.

10 19. A moulding composition as claimed in claim 18, wherein said substance is antimony trioxide.

20. A moulding composition substantially as described in any of Examples 8 to 15. 10

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